

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-026825

(43)Date of publication of application : 27.01.1998

(51)Int.Cl.

G03F 7/00
B41C 1/055
B41N 1/14
G03F 7/004
G03F 7/004
G03F 7/075
G03F 7/075

(21)Application number : 08-180787

(71)Applicant : MITSUBISHI CHEM CORP

(22)Date of filing : 10.07.1996

(72)Inventor : URANO TOSHIYOSHI
HINO ETSUKO

(54) LASER DIRECT PHOTOSENSITIVE PLANOGRAPHIC PRINTING PLATE REQUIRING NO DAMPENING WATER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a laser direct photosensitive planographic printing plate requiring no dampening water and excellent in photosensitivity, ink receptivity and safety by incorporating nitrocellulose having a specified nitrification degree and a specified average polymn. degree into a photosensitive layer.

SOLUTION: This photosensitive planographic printing plate has a photosensitive layer contg. at least a near IR absorber and a silicone rubber layer on the substrate in this order from the substrate side and contains nitrocellulose having a nitrification degree of 2-13 and an average polymn. degree of 20-200 in the photosensitive layer by 5-80wt.%, preferably 10-70wt.% of the total solid content of the layer. The silicone rubber layer preferably contains linear organosiloxane having hydroxyl groups at both terminals by 80 to <98wt.% of the total solid content of the layer and a reactive silane compd. by 2 to <20wt.% of the total solid content of the layer.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the laser direct dampening water unnecessary photosensitivity lithography version which can form the printing version directly using near-infrared semiconductor laser from digital image data. Furthermore, it is related with the laser direct dampening water unnecessary photosensitivity lithography version which paints a sensitization layer and a silicone rubber layer on this order, and changes on a substrate in detail.

[0002]

[Description of the Prior Art] It follows on the advance of the digital image processing technique using near-infrared semiconductor laser and a computer in recent years. Near-infrared semiconductor laser performs scan exposure on the direct photosensitivity lithography version, without using the silver halide film for the printing versions from the digital image data formed on the computer. Or it forms an image by the water-solution development (wet-developing processing) and engraves after insolubilizing an exposure part, the laser direct platemaking technique which an exposure part is degraded, or forms an image by sublimation and the thing (dry-developing processing) which melting is carried out and is removed, and is engraved attracts attention. There is no need of considering the balance of water and printing ink especially, and printing actuation is easy, and since printed matter is easily producible from digital image data in a short time, the dampening water unnecessary digital printing system with short printing time amount is expected [there is little maculature in early stages of printing, and] as a new printing system.

[0003] Although various attempts are made about the laser direct dampening water unnecessary photosensitivity lithography version used for this dampening water unnecessary digital printing system. For example, paint a photosensitive layer and a silicone rubber layer on a (b) base material at this order, and the heat produced by the ablation of the exposure section of a photosensitive layer is answered. What removes a silicone rubber layer by melting, volatilization, or combustion to coincidence (JP,7-164773,A, this 6- 186750, this 6- 199064, this 7- 309001), The heat produced by the ablation of the exposure section of a (b) photosensitivity layer is answered. What is ground after degrading a silicone rubber layer and reducing an adhesive property with a base material (JP,6-55723,A, this 6- 55869, this 6- 92050), (Ha) The thing (JP,51-66008,A) which makes the toner image of ink impression nature form by the xerography on the base material which prepared the silicone rubber layer is known. Since that to which the method of (b) has image formation processing simpler than that, and image quality was [among these] also usually more superior is easy to be obtained, it is thought that it is more suitable.

[0004] However, the laser direct dampening water unnecessary photosensitivity lithography version using the ablation of the above-mentioned (b) has low sensibility, and the large-scale laser light source is required for it, and it had problems, like a laser exposure process takes long duration. Moreover, in order to raise sensibility, the approach of adding autooxidation nature resin, such as a nitrocellulose ingredient, in a photosensitive layer etc. is tried (JP,50-158405,A). However, as for effectiveness, the safety and ink impression nature of a certain thing tended to fall to improvement in sensibility, and usual

nitrocellulose resin was a problem.

[0005]

[Problem(s) to be Solved by the Invention] This invention tends to offer the laser direct dampening water unnecessary photosensitivity lithography version which was excellent in sensitization sensibility and was excellent in both ink impression nature and safety.

[0006]

[Means for Solving the Problem] The summary of this invention consists in the laser direct dampening water unnecessary photosensitivity lithography version characterized by containing the nitrocellulose whenever [whose / nitrification] are 2-13 and, whose average degree of polymerization is 20-200 in this photosensitive layer in the laser direct dampening water unnecessary photosensitivity lithography version which has the photosensitive layer which contains a near-infrared absorbent at least from this substrate on a substrate, and a silicone rubber layer in this order.

[0007]

[Embodiment of the Invention] This invention is further explained to a detail below. As a substrate used in this invention, it has the flexibility which can be set to the usual monotonous printing machine, and if the load applied at the time of printing can be borne, anythings can be used and it will not be limited, especially including lamination. For example, plastic film, such as metal plates, such as papers, such as coat paper, and an aluminum plate, or polyethylene terephthalate, can be mentioned as an example. Among these, polyethylene terephthalate, an aluminum plate or aluminium foil, and other composites are desirable, and this substrate is the purpose which heightens the ablation effectiveness of a sensitization layer and a silicone rubber layer, or it makes this substrate vapor-deposit metals, such as aluminum and chromium, it can perform mirror plane polishing processing, and can also prepare a reflexible front face to near-infrared light.

[0008] The board thickness of this substrate is usually 20 micrometers - 0.5mm preferably 10 micrometers - 1mm. The photosensitive layer used in this invention answers the heat which produces the ablation of a photosensitive layer by it at the same time it removes a lifting photosensitivity layer by changing near-infrared laser light into absorption and heat efficiently, attracts the ablation of a silicone rubber layer, and contains melting and the near-infrared absorbent which has the function to make the pressure in the case of the ablation of a photosensitive layer remove this by making it volatilize or burn.

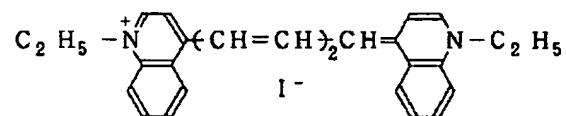
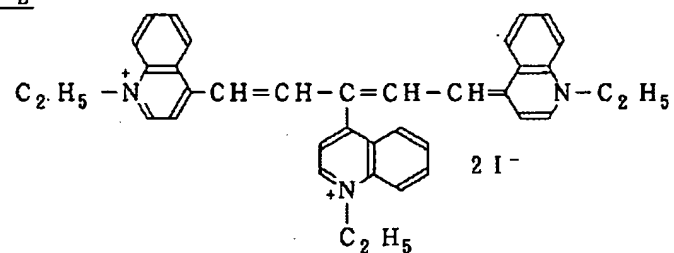
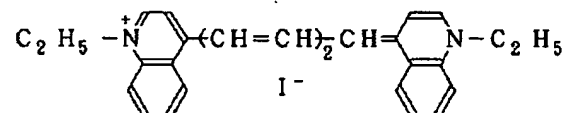
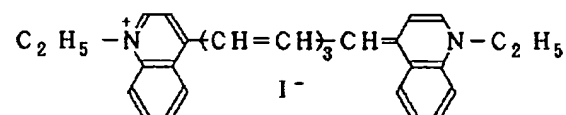
[0009] Although this near-infrared absorbent can be used without absorbing near-infrared light, having the function to transform light energy into heat energy, and especially that limiting, specifically, organic, an inorganic pigment, organic coloring matter, a metal, etc. can be mentioned. Still more specifically For example, metal; titanium oxide, such as carbon black (color black FW2 and FW20, pudding tex V, etc. which is product of MA-7, MA-100, MA-220, #5, #10, and Degussa which is product of Mitsubishi Chemical); graphite; titanium, and chromium, Metallic carbide; metal borides, such as metallic-oxide; titanium carbide, such as tin oxide, a zinc oxide, a vanadium oxide, and tungstic oxide; The inorganic black pigment indicated by JP,4-322219,A, Black, such as a black pigment of an azo system, RIONORU Green 2YS, and green pigments 7, and which green organic pigment are used. Moreover, the coloring matter which has absorption is also used for the near infrared region indicated by the laser coloring matter catalog which the catalog which "special function coloring matter" (Ikemori and Sumiya edit, the 1986 CMC Co., Ltd. issue) "chemistry of functional coloring matter" (Higaki edit, the 1981 CMC Co., Ltd. issue) "coloring matter handbook" (big river, Hirashima, Matsuoka, Kitao edit, Kodansha issue) Japan Sensitizing dye Lab published in 1995, and ExcitonInc. published in 1989. furthermore, JP,3-97590,A -- said -- 97591 -- said -- 63185 -- said -- 26593 -- said -- 97589 and JP,2-2074,A -- said -- the coloring matter which has absorption is also used for near infrared regions, such as organic-coloring-matter and IRby Nippon Kayaku Co., Ltd. 820B which has absorption in the near infrared region indicated by 2075 and these 2076 grades. Some of such near-infrared absorbents are concretely shown in the 1st table of the following.

[0010]

[Table 1]

第 1 表

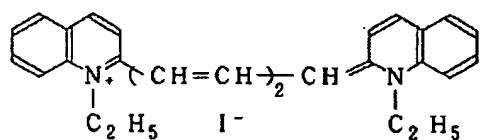
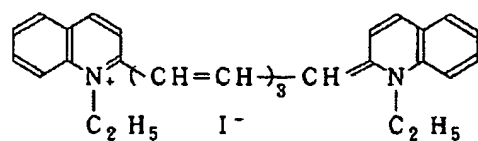
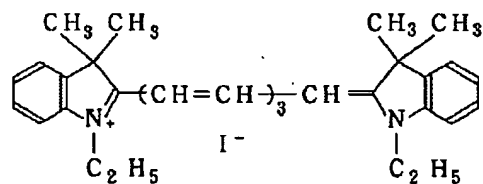
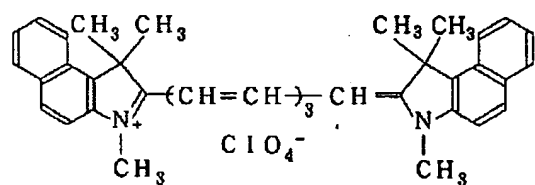
近赤外領域に吸収を有する色素及び顔料

S-1S-2S-3S-4

[0011]

[Table 2]

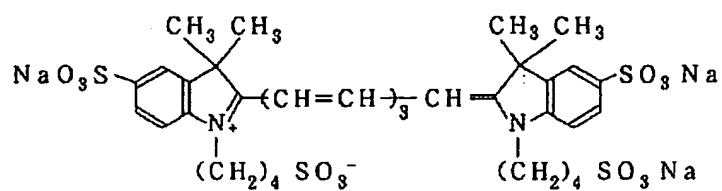
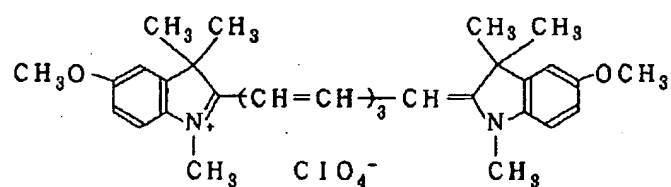
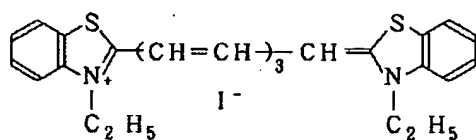
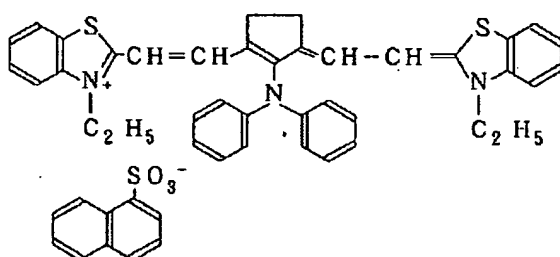
第 1 表 (つづき)

S-5S-6S-7S-8

[0012]

[Table 3]

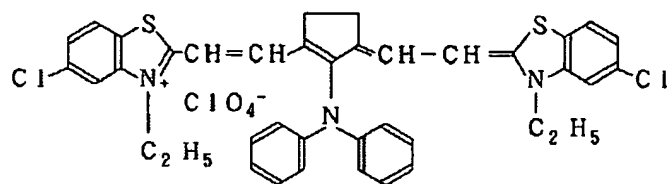
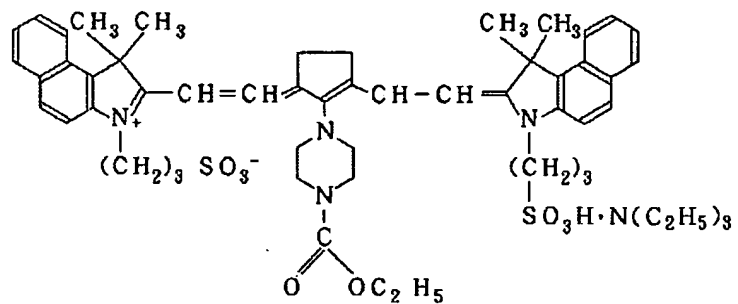
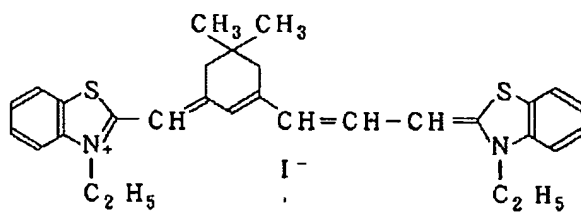
第 1 表 (つづき)

S-9S-10S-11S-12

[0013]

[Table 4]

第 1 表 (つづき)

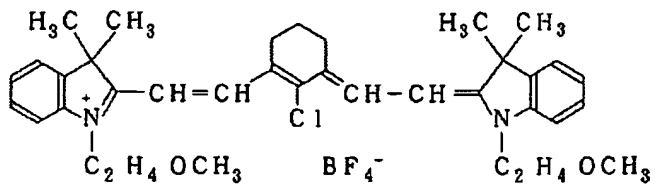
S-13S-14S-15

[0014]

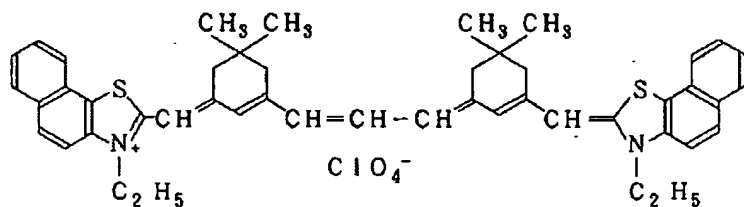
[Table 5]

第 1 表 (つづき)

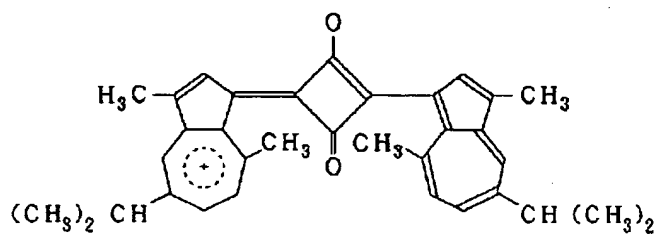
S-16



S-17



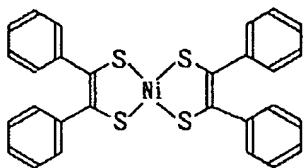
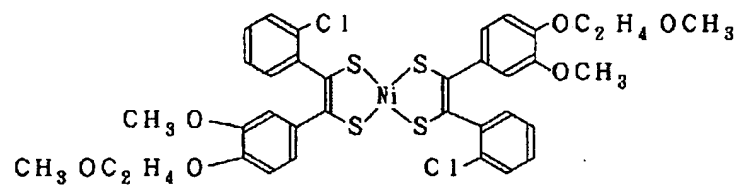
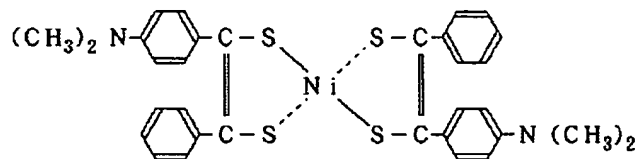
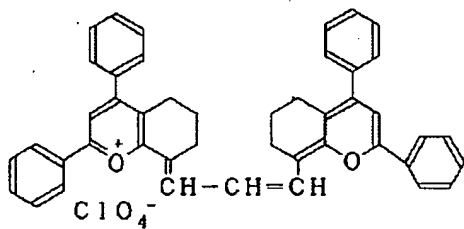
S-18



[0015]

[Table 6]

第 1 表 (つづき)

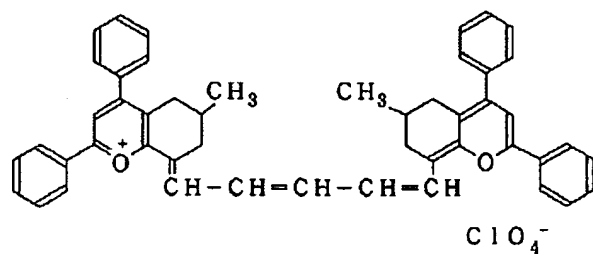
S-19S-20S-21S-22

[0016]

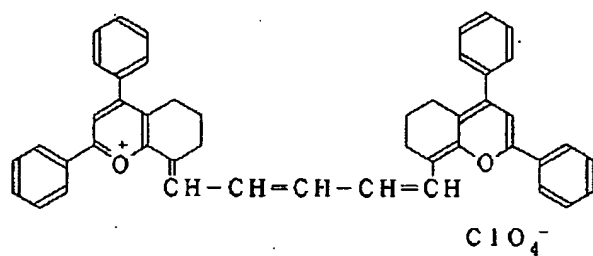
[Table 7]

第 1 表 (つづき)

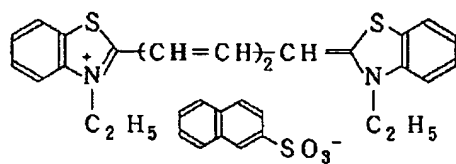
S-23



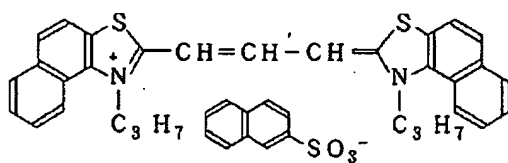
S-24



S-25



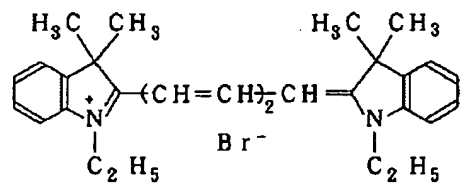
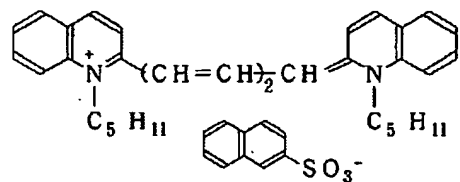
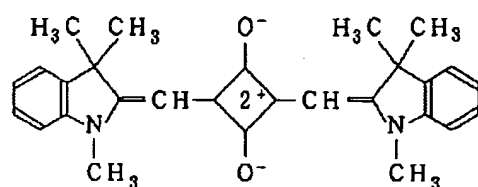
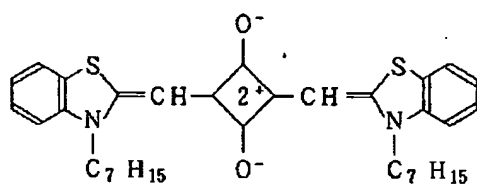
S-26



[0017]

[Table 8]

第 1 表 (つづき)

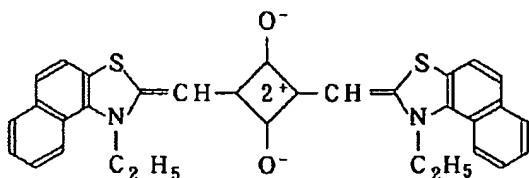
S-27S-28S-29S-30

[0018]

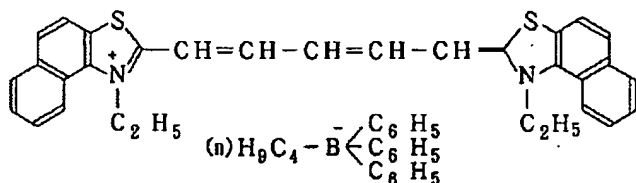
[Table 9]

第 1 表 (つづき)

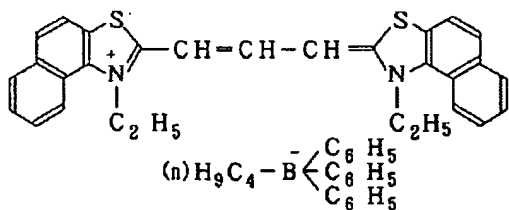
S-31



S-32



S-33



[0019]

[Table 10]

S-34 Poly methine coloring matter; IR-820B (Japanese powder company make)

S-35 Nigrosine coloring matter; Colour Index Solvent Black 5 S-36 Nigrosine coloring matter; Colour Index Solvent Black 7 S-37 Nigrosine coloring matter; Colour Index Acid Black 2 S-38 Carbon black; MA-100 (Mitsubishi Chemical make)

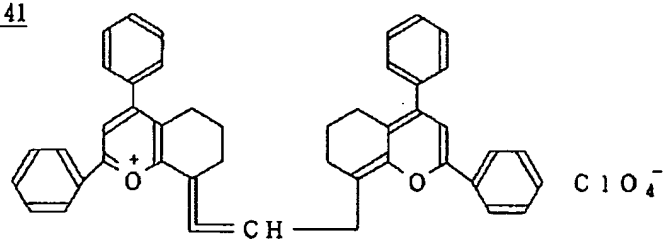
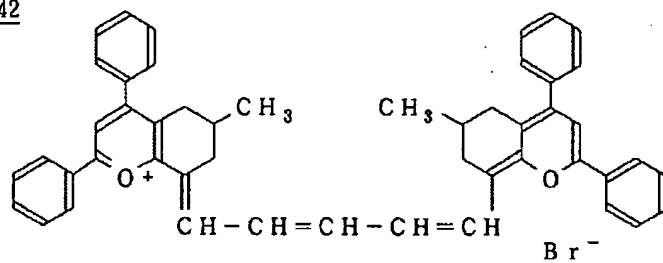
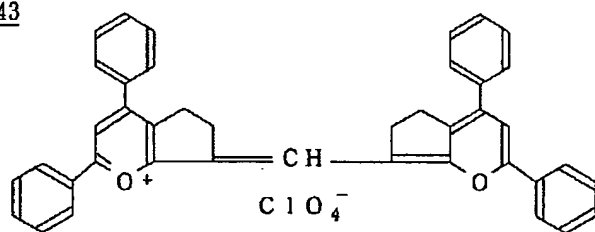
S-39 Titanium monoxide; black-titanium-oxide 13M (MITSUBISHI MATERIALS CORP. make)

S-40 Titanium monoxide; black-titanium-oxide 13B (MITSUBISHI MATERIALS CORP. make)

[0020]

[Table 11]

第1表 (つづき)

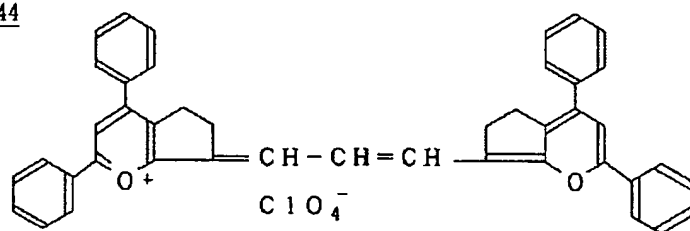
S-41S-42S-43

[0021]

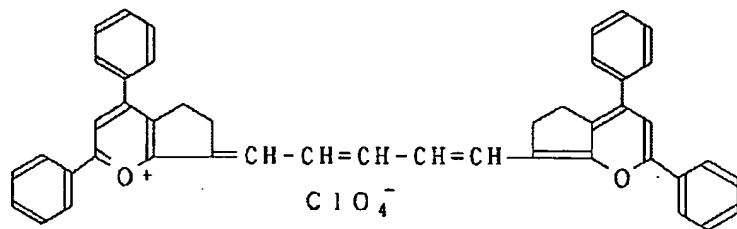
[Table 12]

第1表 (つづき)

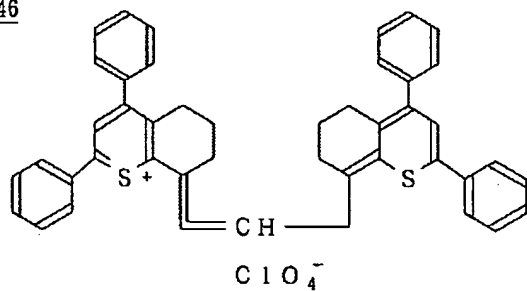
S-44



S-45



S-46

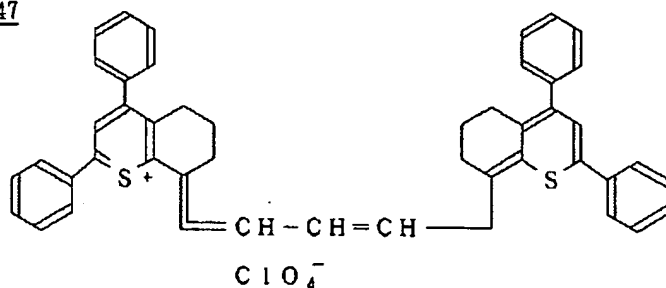


[0022]

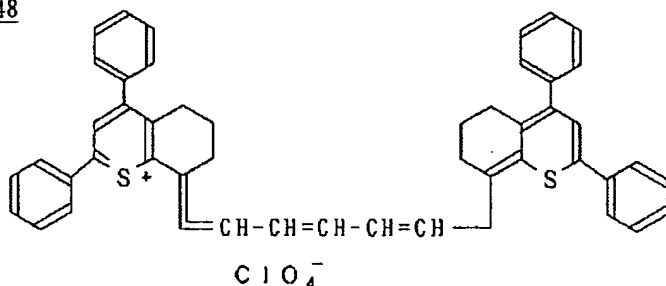
[Table 13]

第1表 (つづき)

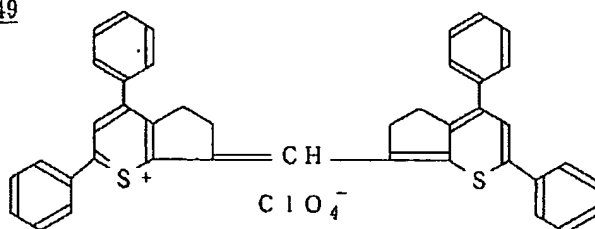
S-47



S-48



S-49



[0023] these near-infrared absorbent is independent -- or -- two or more -- mixing -- the inside of a photosensitive layer spreading solution -- the dissolution -- or it can be made to be able to distribute, can blend and can use. the rate of combination in the inside of the photosensitive layer of this near-infrared absorbent -- 5- of all photosensitive layer solid content -- it is 10 - 70 % of the weight preferably 80% of the weight. If the rate of combination of a near-infrared absorbent is remarkably low, laser light cannot be absorbed enough but the effectiveness of ablation will tend to fall.

[0024] The nitrocellulose used for this invention decomposes near-infrared laser light with the heat which the near-infrared absorbent absorbed and was generated, and has the function which promotes removal of the laser exposure section among a photosensitive layer and a silicone rubber layer by generating efficient low-molecular gas. This nitrocellulose nitrates the natural cellulose refined by the usual approach with a mixed acid, and the part of three hydroxyl groups which exist in the glucopyranose ring which is the configuration unit of a cellulose obtains a nitro group a part or by introducing all.

[0025] Whenever [nitrification-nitrocellulose used for this invention] are 2-13, are 10-12.5 preferably, and are 11-12.5 still more preferably. Here, whenever [nitrification] expresses weight % of the nitrogen atom in a nitrocellulose. If whenever [nitrification] is remarkably high, although the facilitatory effect of ablation will be heightened, it is in the inclination for room temperature stability to fall, and a nitrocellulose serves as explosivity, and risk follows on the handling of the nitrocellulose at the time of producing the printing version. If whenever [nitrification] is remarkably low, the facilitatory effect of ablation will not be acquired enough.

[0026] Moreover, the polymerization degree of this nitrocellulose is 20-200, and is 25-150 preferably. When polymerization degree is remarkably high, it is in the inclination for removal of a silicone rubber layer to become imperfect and for the ink impression nature of a laser exposure part (image part) to become a defect. If polymerization degree is remarkably low, while the paint film nature of a photosensitive layer will become a defect, it is in the inclination exfoliation of a silicone rubber layer becomes easy to produce.

[0027] The rate of combination in the inside of the photosensitive layer of this nitrocellulose is 30 - 70 % of the weight still more preferably ten to 70% of the weight preferably five to 80% of the weight to a photosensitive **** formed element.

[0028] In the photosensitive layer used by this invention, an organic high polymer can be added in order to heighten the paint film nature, the compatibility with a near-infrared absorbent, the film reinforcement in a photosensitive layer, and the effectiveness of ablation other than the above-mentioned near-infrared absorbent and a nitrocellulose.

[0029] As this organic high polymer, for example Partial saturation acids, such as an acrylic acid (meta) and an itaconic acid, Acrylic-acid alkyl, acrylic-acid (meta) phenyl, acrylic-acid (meta) benzyl, (Meta) The polymer of the alkyl methacrylate represented by copolymer; polymethylmethacrylate with styrene, alpha methyl styrene, etc., or acrylic-acid alkyl; (meta) Acrylic-acid alkyl and acrylonitrile, The cellulose denaturation object; polyethylene oxide; polyvinyl pyrrolidone which has a carboxyl group in the copolymer; side chain of copolymer; acrylonitrile, and a vinyl chloride and a vinylidene chloride with a vinyl chloride, a vinylidene chloride, styrene, etc.; A phenol, o-, m-, p-cresol, And/or, KISHIREZORU and an aldehyde, Novolak resin; obtained by the condensation reaction with an acetone etc. polyether [of epichlorohydrin and bisphenol A]; -- fusibility nylon; -- polyvinylidene chloride; -- chlorinated-polyolefins; -- copolymer [of a vinyl chloride and vinyl acetate]; -- polymer [of vinyl acetate]; -- copolymer [of acrylonitrile and styrene]; -- a butadiene with acrylonitrile And copolymer [with styrene]; Polyvinyl alkylether; Polyvinyl alkyl ketone; polystyrene; -- polyurethane; -- polyethylene terephthalate isophthalate; -- acetyl-cellulose; -- acetyl PUROI oxycellulose; -- acetyl butoxy cellulose; -- nitrocellulose; -- celluloid; -- a polyvinyl butyral etc. is used. the rate of combination in the photosensitive layer of this organic high polymer -- 0- of all photosensitive layer solid content -- it is 5 - 40 % of the weight still more preferably two to 50% of the weight preferably 60% of the weight.

[0030] Moreover, the various additives which have a hydrophobic radical in order to raise printing ink impression nature into the above-mentioned photosensitive layer, For example, p-octyl phenol formalin novolak resin, p-butylphenol formalin novolak resin, Denaturation novolak resin, such as p-t-butylphenol benzaldehyde resin and rosin denaturation novolak resin, For furthermore, the purpose which adds the surface active agent of o-naphthoquinonediazide sulfonate of these denaturation novolak resin, and a fluorine system, or heightens the effectiveness of ablation Nitro compounds, such as a nitrocellulose of autooxidation nature, a sodium nitrate, Peroxides, such as nitrates, such as an ammonium nitrate, a benzoyl peroxide, and perbenzoic-acid ester, Or azo compounds, such as an AZOJI carvone amide of fizz, and azobisisobutyronitril, Nitroso compounds, such as an N and N'-dinitro pentamethylene tetramine, The total solids of a photosensitive layer are received in sulfonylhydrazide compounds, such as a p-tosyl hydrazine, p, and p'-oxy-screw (benzene sulfo hydrazine), etc. 0.1 - 30 % of the weight, Preferably, 0.2 to 20% of the weight, it can add 0.5 to 10% of the weight, and can use still more preferably.

[0031] Moreover, the photosensitive layer of this invention can be made to contain particles other than the above-mentioned particle, such as silicon oxide and titanium oxide, in order to make a particle 5 micrometers or less with low thermoelectrical ****, such as a calcium carbonate, a magnesium carbonate, a zirconium dioxide, and KARION, contain in order to raise the effectiveness of ablation or to raise the film reinforcement of a photosensitive layer. the rate of combination of this particle -- 0- of the total solids of a photosensitive layer -- it is 0 - 25 % of the weight preferably 50% of the weight. Moreover, 0.05-10 micrometers of 0.1-5 micrometers of thickness of the photosensitive layer used by this invention are 0.3-2 micrometers still more preferably preferably.

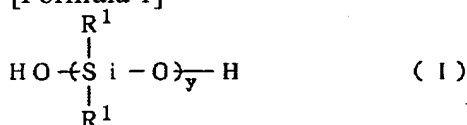
[0032] Although the silicone rubber layer used for this invention can be suitably chosen from a well-

known thing which is indicated by above mentioned JP,7-164773,A etc., the thing of the condensation bridge formation type which is explained below and which stiffens a silicone rubber layer constituent by the condensation reaction, and two types of the addition bridge formation type which stiffens a silicone rubber layer constituent by the addition reaction is used preferably.

[0033] the line to which the silicone rubber layer of the condensation bridge formation type used in this invention has a hydroxyl group in both ends -- the reactant silane compound in which construct a bridge over with organopolysiloxane and this organopolysiloxane, and a silicone rubber layer is made to form is included as an indispensable component. the line which has a hydroxyl group in the both ends used by this invention -- as an ORUGA polysiloxane -- the line of the following general formula (I) -- organopolysiloxane is mentioned.

[0034]

[Formula 1]



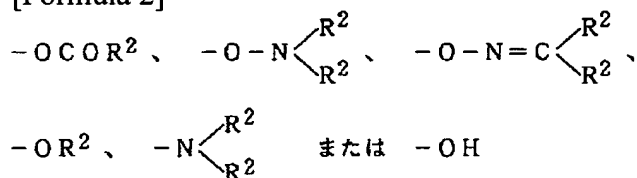
[0035] (Two R1 shows respectively independently a hydrogen atom, a methyl group, a phenyl group, and a vinyl group among a formula, and y shows one or more integers.)

Inside R1 of the compound expressed with the above-mentioned general formula (I) What is a methyl group is desirable. The weight average molecular weight (it abbreviates to Mw hereafter) of this organopolysiloxane is 5,000-1,000,000, and is 10,000-1,000,000 preferably. If Mw is remarkably low, the film reinforcement of a silicone rubber layer will fall, printing-proof nature becomes low, and if Mw is remarkably high, the removal effectiveness of the silicone rubber layer by ablation will fall, and they are a lifting and a cone about a sensibility fall and the fall of image repeatability.

[0036] moreover, the line to which the reactant silane compound used for this invention has a hydroxyl group in said both ends -- it is a with a molecular weight of 2,000 or less which has at least two or more functional groups which can react with the hydroxyl group of organopolysiloxane and can carry out lifting bridge formation of the condensation, such as a decarboxylation type, a deoxime mold, a dealcoholization mold, a deamination mold, or a dehydration mold, reactant silane compound. The functional group specifically expressed with following each type as this functional group is mentioned.

[0037]

[Formula 2]



[0038] (Among the formula, although R2 shows the alkyl group of carbon numbers 1-5, when there is two R2 in the same atomic group, even if each is the same, it may differ.)

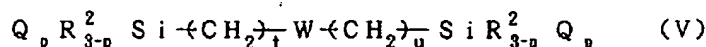
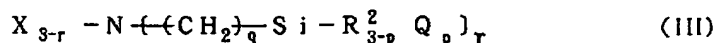
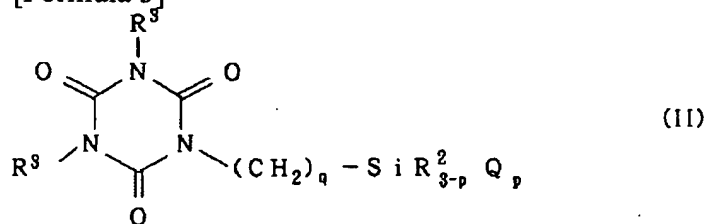
A functional group is [among these] desirable at an acyloxy radical (-OCOR2), in order that the number of functional groups may set three or more things to three or more things, a functional group may set after the desiccation processing after spreading by the alkoxy group (-OR2) and the number of functional groups may form a silicone rubber layer for a short time. Furthermore, for the number of functional groups, three or more things or a functional group is [a functional group / the numbers of functional groups] six or more things in an alkoxy group preferably at an acetoxy radical.

[0039] As this reactant silane compound, it is for example, the following general formula (II). The compound expressed with - (V) can be mentioned. the line to which the inside Q of a formula has a hydroxyl group in said both ends carried out -- what was chosen from the hydroxyl group of organopolysiloxane and the functional group which reacts shall be expressed, and it shall have Q in [at

least two] 1 molecule

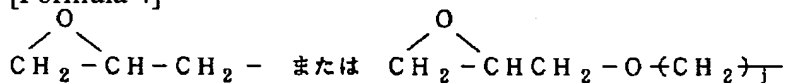
[0040]

[Formula 3]

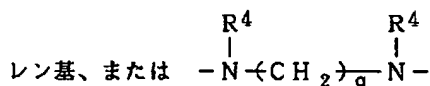


[0041] the inside of a formula, and X -- the alkyl group of carbon numbers 1-5, a phenyl group, a vinyl group, H₂N-(CH₂)_h-, CH₂=C(CH₃)CO-, CH₂=CHCO-, and [0042]

[Formula 4]



を示し、Wは酸素原子、硫黄原子、-SSSS-、炭素数1～10のアルキ



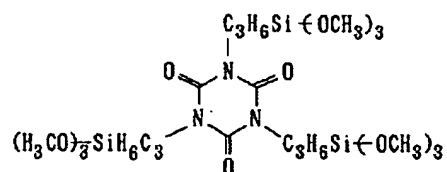
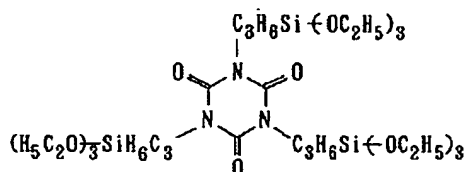
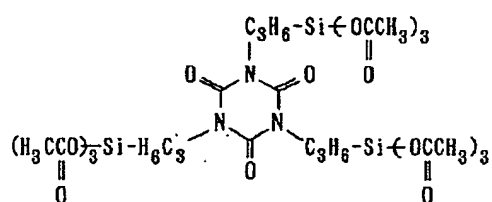
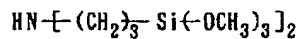
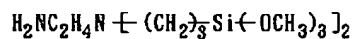
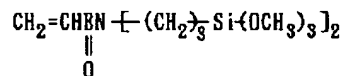
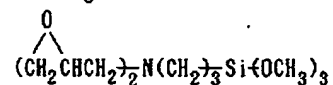
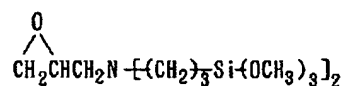
[0043] An example and R₂ The alkyl group of carbon numbers 1-5 is shown like the above, and it is R₃. An allyl group or -(CH₂)_q-SiR_{23-p}Q_p It is shown and is R₄. Although a hydrogen atom, the alkyl group of carbon numbers 1-5, or a phenyl group is shown R₂, R₃, and R₄ When two or more each exists in the same intramolecular, you may differ, even if two or more of the each is the same, and h, j, and q show the integer of each 1-5, p and r show the integer of each 1-3, s shows the integer of 2-4, and t and u show the integer of each 0-5.

Although a still more concrete example is given to the 2nd table about the reactant silane compound used for this invention, it is not limited to what is these-illustrated.

[0044]

[Table 14]

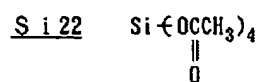
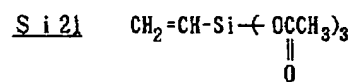
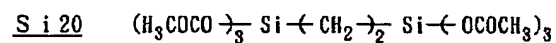
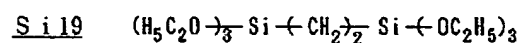
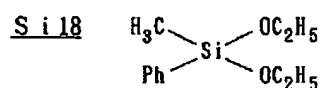
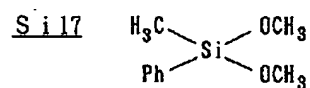
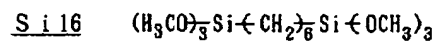
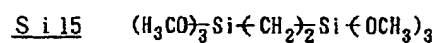
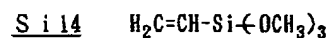
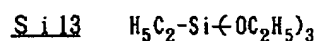
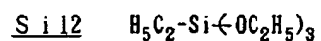
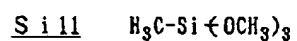
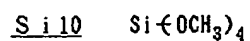
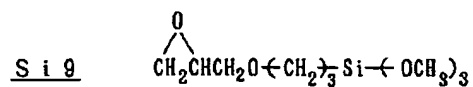
第 2 表

Si 1Si 2Si 3Si 4Si 5Si 6Si 7Si 8

[0045]

[Table 15]

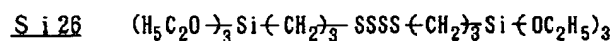
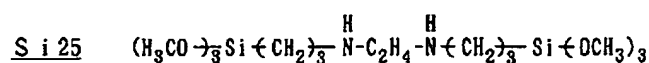
第 2 表 (つづき)



[0046]

[Table 16]

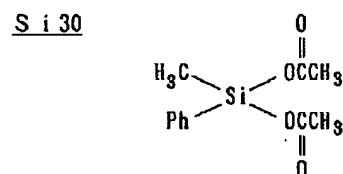
第 2 表 (つづき)



Si 27 メチルトリス (アセトンオキシム) シラン、

Si 28 ビニルトリ (メチルエチルケトオキシム) シラン、

Si 29 メチルトリ (メチルエチルケトオキシム) シラン、



[0047] In order that the silicone rubber layer of the condensation bridge formation type used for this invention may raise the reaction effectiveness of the condensation crosslinking reaction of organopolysiloxane and a reactant silane compound in which it has a hydroxyl group to the above-mentioned both ends, it mixes suitably condensation catalysts, such as an organic carboxylic acid, titanate, stannic acid ester, the aluminum organic ether, and a platinum system catalyst, and makes it harden by performing a condensation reaction.

[0048] The rate of combination in the inside of the silicone rubber layer of the organopolysiloxane which has a hydroxyl group in the both ends used in this invention, a reactant silane compound, and a condensation catalyst The organopolysiloxane which has a both-ends hydroxyl group to the solid content of all silicone rubber layers 80 - 98 % of the weight, A reactant silane compound is 2 - 7 % of the weight, and a condensation catalyst is 2 - 20 % of the weight usually 0.1 - 1 % of the weight still more preferably 0.1 to 3% of the weight 0.05 to 5% of the weight still more preferably two to 15% of the weight 85 to 98% of the weight preferably.

[0049] If the rate of a reactant silane compound or a condensation catalyst is remarkably high, ink rebounding nature will fall, and removal of the silicone rubber layer at the time of ablation becomes difficult, and sensibility and image repeatability fall. Moreover, if remarkably low on the contrary, the film reinforcement of a silicone rubber layer will fall and printing endurance will fall.

[0050] The silicone rubber layer of the condensation bridge formation type used for this invention can be made to contain preferably polysiloxanes other than the polyorganosiloxane which has a hydroxyl group three to 12% of the weight two to 15% of the weight to silicone rubber layer total solids to the above-mentioned both ends in order to raise the ink rebounding nature of a silicone rubber layer. As this polysiloxane, the poly dimethylsiloxane of Mw 10,000-1,000,000 by which both ends were trimethylsilylated etc. is mentioned.

[0051] Next, the silicone rubber layer of the addition bridge formation type used for this invention contains the organopolysiloxane which has at least two aliphatic series partial saturation radicals in 1 molecule, and the organopolysiloxane in which construct a bridge over with this organopolysiloxane and

a silicone rubber layer is made to form and which has at least two Si-H association in 1 molecule as an indispensable component.

[0052] The organopolysiloxane which has at least two aliphatic series partial saturation radicals in 1 molecule used for this invention has the desirable shape of a chain, although any of the shape of a chain, annular, and the letter of branching are sufficient as the structure. As an example of an aliphatic series partial saturation radical, alkynyl groups, such as cyclo alkenyl radical; ethynyl groups, such as alkenyl radical; cyclo pentenyl radicals, such as a vinyl group, an allyl group, a butenyl group, a pentenyl radical, and a hexenyl radical, a cyclohexenyl group, a cycloheptenyl group, and a cyclo octenyl group, a propynyl radical, a butynyl radical, a cutting-pliers nil radical, and a hexynyl group, etc. are mentioned. The alkenyl radical which has an unsaturated bond at the end from a reactant point is [among these] desirable, and especially a vinyl group is desirable. Moreover, the substituent of the remainders other than an aliphatic series partial saturation radical has a desirable methyl group, in order to obtain good printing ink rebounding nature.

[0053] Mw(s) of organopolysiloxane which have at least two aliphatic series partial saturation radicals in 1 molecule are usually 500-500,000, and are 1,000-3,000,000 preferably. If Mw is remarkably low, the reinforcement of a silicone rubber layer falls, it will be easy to take lessons for a blemish from a silicone rubber layer at the time of printing, the printing ink rebounding nature of the part will fall, ink will become easy to adhere, and it will become the cause of printing dirt. Moreover, when Mw is remarkably high, removal of the silicone rubber layer by ablation becomes poor, and they are a lifting and a cone about the fall of sensibility, and the fall of image repeatability.

[0054] The organopolysiloxane which has at least two Si-H association in 1 molecule used for this invention has the desirable shape of a chain, although any of the shape of a chain, annular, and the letter of branching are sufficient as the structure. The percentage that Si-H association may have in the end of a siloxane frame or middle any, and the hydrogen atom to the total of a substituent occupies is usually 1 - 60%, and is 2 - 50% preferably. Moreover, the substituent of the remainders other than a hydrogen atom has a desirable methyl group, in order to obtain good printing ink rebounding nature. Mw(s) of organopolysiloxane which have at least two Si-H association in 1 molecule are usually 300-300,000, and are 500-200,000 preferably. When Mw is remarkably high, they are a lifting and a cone about the fall of sensibility, and the fall of image repeatability.

[0055] In order to carry out the addition reaction of the organopolysiloxane which has at least two aliphatic series partial saturation radicals in the above-mentioned 1 molecule, and the organopolysiloxane which has at least two Si-H association in 1 molecule, an addition reaction catalyst is usually used. Although it can be chosen as arbitration from well-known things as this addition reaction catalyst, a platinum system catalyst is desirable and one sort or two sorts or more of mixture chosen from a platinum metal and a platinum group system compound is used. As a platinum metal, the simple substance (for example, platinum black) of platinum, the simple substance (for example, palladium black) of palladium, the simple substance of a rhodium, etc. are illustrated. Moreover, as a platinum group system compound, chloroplatinic acid, a platinum-olefin complex, a platinum-alcoholic complex, a platinum-ketone complex, platinum, the complex of a vinyl siloxane and tetrakis (triphenyl phosphine) platinum, tetrakis (triphenyl phosphine) palladium, etc. are illustrated. Also among these, especially the thing that dissolved chloroplatinic acid or a platinum-olefin complex in an alcohols solvent, ketones, the ethers solvent, the hydrocarbon system solvent, etc. is desirable.

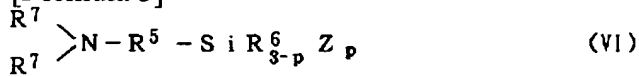
[0056] The rate of combination of the class product which forms the above mentioned silicone rubber layer The organopolysiloxane which has at least two aliphatic series partial saturation radicals in 1 molecule to the total solids of a silicone rubber layer The organopolysiloxane which is 85 - 98 % of the weight preferably, and it has with at least two Si-H association in 1 molecule 80 to 98% of the weight Two to 20% of the weight, it is 2 - 15 % of the weight preferably, and an addition reaction catalyst is 0.0001 - 5 % of the weight preferably 0.00001 to 10% of the weight.

[0057] If the rate of combination of the organopolysiloxane which has at least two Si-H association in 1 molecule is remarkably low, the film reinforcement of a silicone rubber layer will fall, printing ink rebounding nature and printing-proof nature fall, and if the rate of combination is remarkably high,

sensibility and image repeatability will fall. Moreover, in the silicone rubber layer of the addition bridge formation type used for this invention, the amino system organic silicon compound which has the hydrolysis nature machine with which it is expressed by the following general formula (VI) can be added in order to raise the film reinforcement of a silicone rubber layer other than the above-mentioned presentation further.

[0058]

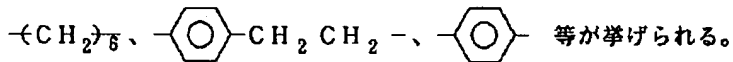
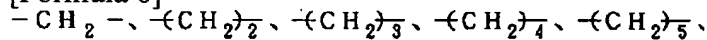
[Formula 5]



[0059] (Among a formula (VI), Z shows a hydrolysis nature machine, R5 shows a divalent hydrocarbon group, R6 shows the hydrocarbon group by which univalent may be permuted, two R7 shows the radical expressed respectively independently with a hydrogen atom, the hydrocarbon group by which univalent may be permuted, or -R5-SiR63-pZp, and p shows the integer of 1-3.)

[0060] As a hydrolysis nature machine expressed with Z, acyloxy radicals, such as aryloxy group; acetyloxy radicals [, such as an alkenyloxy radical; phenoxy group,], such as alkoxy group; 2-propenyloxy radicals, such as a methoxy group, an ethoxy radical, and a propoxy group, etc. are mentioned. A methoxy group, an ethoxy radical, and an acetyloxy radical are [among these] desirable from points, such as stability and hardenability. R5 As a hydrocarbon group of bivalence, it is [0061].

[Formula 6]



これらのうち $-(\text{CH}_2)_3-$

[0062] ** -- it is desirable. R6 And R7 as the hydrocarbon group by which monovalence may be permuted among the substituents expressed -- for example Alkyl groups, such as a methyl group, an ethyl group, a propyl group, and butyl; A cyclo propyl group, Cyclo butyl, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, Cycloalkyl radicals, such as a cyclo octyl radical; A vinyl group, an allyl group, a butenyl group, Alkenyl radicals, such as a pentenyl radical and a hexenyl radical; A cyclo pentenyl radical, Cyclo alkenyl radicals, such as a cyclohexenyl group, a cycloheptenyl group, and a cyclo octenyl group; permutation alkyl groups, such as a glycidoxy propyl group, an acryloxypropyl radical, a methacryloxypropyl radical, and an aminoethyl radical, etc. are mentioned. The point of hardenability to R6 And R7 A vinyl group, an allyl group, a glycidyl group, an methacrylic radical, or gamma-glycidoxy propyl group is desirable.

[0063] As an example of this amino system silicon compound, for example, 3-[N-allyl compound-N-(2-aminoethyl)] aminopropyl trimethoxysilane, 3-(N-allyl compound-N-glycidyl) aminopropyl trimethoxysilane, 3-(N-allyl compound-N-methacrylic) aminopropyl trimethoxysilane, An N-glycidyl-N and N-bis[3-(methyl dimethoxy silyl) propyl] amine, An N-glycidyl-N and N-bis[3-(trimethoxysilyl) propyl] amine, Aminopropyl trimethoxysilane, an aminopropyl thoria cetyl oxy-silane, A 3-[N-allyl compound-N-(2-aminoethyl)] aminopropyl thoria cetyl oxy-silane, 3-(N-allyl compound-N-glycidyl) aminopropyl thoria cetyl oxy-silane, 3-(N-allyl compound-N-methacrylic) aminopropyl thoria cetyl oxy-silane, etc. are mentioned. These may mix and use two or more kinds.

[0064] The organic silicon compound of this amino system is 0 - 5 % of the weight preferably zero to 10% of the weight to the total solids of a silicone rubber layer. Moreover, in the silicone rubber layer of the addition bridge formation type used for this invention, in case a silicone rubber layer is painted, a concrete retarder can be added in order to prevent rapid hardening of a silicone layer presentation. It can be chosen as arbitration out of the silyl ghost of the acetylene series alcohol generally known as a concrete retarder, a maleate, and acetylene series alcohol, the silyl ghost of a maleic acid, triallyl isocyanurate, a vinyl siloxane, etc.

[0065] Although the addition of this concrete retarder changes with desired cure rates, it is usually the 0.0001 - 1.0 weight section to the total solids of a silicone rubber layer. Minerals bulking agents, such as a silica, titanium oxide, and an aluminum oxide, may be added in a silicone rubber layer the condensation bridge formation type used for above-mentioned this invention, and addition bridge formation type, and especially a silica is preferably used for it in order to raise the reinforcement. As such a bulking agent, a thing with a mean particle diameter [the point of dispersibility or distributed stability to] of 500 micrometers or less is desirable.

[0066] These silicone rubber layers are excellent in printing ink rebounding nature and printing-proof nature, are further removed easily by ablation, are high sensitivity and have the function to give high image repeatability. As for the scratch reinforcement of this silicone rubber layer, it is desirable that they are 10-100g. However, when scratch reinforcement moves a 0.2mm sapphire needle at 10cm speed for /, adding a load on the printing version, it expresses a load (g) required since a scratch occurs. If scratch reinforcement is the above-mentioned range, printabilities, such as printing ink rebounding nature, printing-proof nature, sensibility, and image repeatability, will become good. 0.1-10 micrometers of 0.2-5 micrometers of thickness of the silicone rubber layer used in this invention are 0.3-2 micrometers still more preferably preferably.

[0067] After the photosensitive layer constituent and silicone rubber layer constituent which were indicated above dissolve in a suitable solvent and apply a solution, nothing, and this to a base material on said substrate with various kinds of coaters, such as a wire bar, a spinner, and a roll coater, it can dry and they can form a photosensitive layer and a silicone rubber layer, respectively. As a spreading solvent of a photosensitive layer, for example Ketones, such as a methyl ethyl ketone and a cyclohexanone Ester, such as butyl acetate, amyl acetate, and ethyl propionate, toluene, A xylene, monochlorobenzene, a carbon tetrachloride, a trichloroethylene, Hydrocarbons, such as trichloroethane, halogenated hydrocarbon, methyl cellosolve, To ether, such as ethylcellosolve and a tetrahydrofuran, and a pan, propylene-glycol-monomethyl-ether acetate, The thing of daily use, such as vent KISON and dimethylformamide, can be used. As a spreading solvent of a silicone rubber layer n-hexane, a cyclohexane, the petroleum ether, the product made from Aliphatic-hydrocarbons Exxon Chemistry: The mixed solvent of Isopar E, H, and G and these solvents, and the above-mentioned photosensitive layer spreading solvent etc. can be used.

[0068] Moreover, if needed, the printing version of this invention is the purpose which protects a silicone rubber layer, and can laminate and prepare metal sheets, such as various mold-release characteristic sheets plastic, such as a polypropylene sheet, a polyethylene sheet, and mold release processing polyethylene terephthalate, mold release processing paper, aluminum, iron, and copper, etc. on a silicone rubber layer as an outermost layer. The photosensitive sample which prepared an above-mentioned photosensitive layer and an above-mentioned silicone rubber layer on the substrate Usually, although it is used without after treatment as a printing version after the beam spot which condensed the semiconductor laser light which oscillates 680-1100nm near-infrared light in the diameter of 5-30 micrometer performing scan exposure and carrying out ablation of the exposure part In order to remove the particle of the photosensitive layer generated in the ablation which adhered on this exposed printing version, or a silicone rubber layer After treatment which gives a physical stimulus of a brush, a pad, a supersonic wave, a spray, etc. may be performed supplying a water solution or an organic solvent for a silicone rubber layer front face if needed.

[0069] moreover, as other methods of removing the particle generated in this ablation On the silicone rubber layer of the photosensitive printing version [finishing / exposure of the cover sheet which has an adhesive high front face / layer / silicone rubber], to this particle After laminating so that a silicone rubber front face and an adhesive cover sheet front face may be put together, Before the approach of exfoliating, or exposure, it is this cover sheet, and the cover sheet which passes laser light is laminated like the above, and the approach except the particle on exfoliation and a silicone rubber layer etc. is mentioned after exposure. What prepared adhesive layers, such as silicone rubber, an ionomer, and vinyl acetate, on the radical versions, such as polyethylene terephthalate, polypropylene, a polycarbonate, and paper, as this cover sheet if needed is mentioned.

[0070]

[Example] Although an example explains this invention still more concretely below, this invention is not limited to the following examples.

The photosensitive layer constituent of the following presentation was applied on the substrate shown in examples 1-8, the example 1 of a comparison - the 2 3rd table.

[0071]

[Photosensitive layer constituent]

Near-infrared absorbent: S-41 (compound given in the 1st table) 50 weight sections Nitrocellulose:

Compound given in the 3rd table Loadings given in the 3rd table An organic polymeric material:

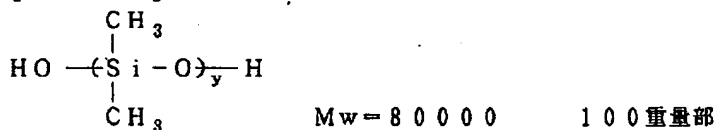
Phenoxy resin (PKH-J, made in Union Carbide)

Loadings given in the 3rd table Spreading solvent: Cyclohexanone It dried for 3 minutes at 85 degrees C after 900 weight sections spreading, and the sensitization layer of 1.5 micrometers of desiccation thickness was prepared. Then, the silicone rubber layer constituent of the following presentation was applied on this photosensitive layer.

[0072] a [silicone rubber layer constituent] -- the line which has a hydroxyl group in both ends -- organopolysiloxane: -- a bottom-type compound (y shows one or more integers)

[0073]

[Formula 7]



[0074]

Reactant silane compound: Compound given in the 3rd table Loadings given in the 3rd table

Condensation catalyst: Dibutyl tin JIRAU rate The 0.8 weight sections Spreading solvent: Isopar E (exon chemistry company make) It dried for 4 minutes at 100 degrees C after 900 weight sections spreading, the silicone rubber layer of 1 micrometer of desiccation thickness was prepared, and the photosensitive printing version was produced.

[0075] This photosensitive printing version was fixed so that a silicone rubber layer might become the rotating drum of 20cm of peripheries outside, and the drum was rotated. Next, on the revolving printing version, the beam diameter of 15 micrometers was made to condense semiconductor laser light (830nm and 30mW) (the Hitachi, Ltd. make, HL8325G), and scan exposure was performed. Then, it evaluated about the following items. The result is shown in the 3rd table.

[0076] Whenever [[whenever / admiration /]] After carrying out scan exposure of the printing version, rotating a rotating drum at various rotational frequencies, this printing version was observed under the 400 times as many microscope as this, and the silicone rubber layer of a laser exposure part evaluated sensibility by the highest scan speed (cm/s) removed. It expresses that it is high sensitivity, so that a scan speed is high.

[0077] [Ink impression nature] The platen of the diameter of 7cm is used for the printing version which gave laser exposure. After scouring the dampening water unnecessary lithography version printing ink (Oriental ink company make, aqualess echo red), the roller to which this ink adhered in the condition of having made it contacting on the printing version with the highest scan speed Both-way migration of this printing version top was carried out 5 times, the ink peak was performed, and ink impression nature was evaluated from the ink impression situation of a laser exposure part.

A: Ink adheres to 90% or more of part of a laser exposure part.

B: Ink adheres to the part of less than 90% 80% or more of a laser exposure part.

C: Ink adheres to the part of less than 70% 50% or more of a laser exposure part.

D: The adhesion part of ink is less than 50% of a laser exposure part.

[0078]

[Table 17]

第 3 表

	基板	ニトロセルロース (※1)	反応性シラン化合物 (※2)	有機高分子物質の 配合量 (※2)	感度 (cm/s)	インク 着肉性	引掻傷 強度 (g)
実施例 1	<u>K-2</u>	<u>N-1</u> (50)	<u>S14</u> (7)	—	100	A	30
実施例 2	<u>K-2</u>	<u>N-2</u> (50)	<u>S14</u> (7)	—	95	A	30
実施例 3	<u>K-2</u>	<u>N-3</u> (50)	<u>S14</u> (7)	—	95	A	30
実施例 4	<u>K-2</u>	<u>N-1</u> (50)	<u>S11</u> (7)	(20)	80	B	38
実施例 5	<u>K-2</u>	<u>N-1</u> (50)	<u>S121</u> (7)	—	100	A	37
実施例 6	<u>K-2</u>	<u>N-1</u> (50)	<u>S123</u> (7)	—	95	A	35

[0079]

[Table 18]

第 3 表 (つづき)

	基板	ニトロセルロース (※1)	反応性シラン化合物 (※2)	有機高分子物質の 配合量 (※2)	感度 (cm/s)	インク 着肉性	引掻傷 強度 (g)
実施例 7	K-1	N-1 (50)	Si1 (7)	—	50	B	38
実施例 8	K-3	N-1 (50)	Si1 (7)	—	70	B	38
比較例 1	K-2	CN-1 (50)	Si4 (7)	—	80	D	30
比較例 2	K-2	CN-2 (50)	Si4 (7)	—	85	D	30

*1: The inside of () expresses weight % to the total solids of a photosensitive layer.

*2: The inside of () expresses weight % to the total solids of a silicone rubber layer.

[0080] The cable address of the column of a substrate expresses the following substrates among the 3rd table, respectively.

K-1; -- with a thickness of 100 micrometers polyethylene terephthalate sheet K-2; -- to both sides of art paper with a thickness of 100 micrometers A foaming polyethylene terephthalate sheet with a thickness of 38 micrometers is laminated using urethane system adhesives (bamboo NETO A-7 by Takeda Chemical, Ltd., and the bamboo rack A-367 by Takeda Chemical, Ltd. H mixed liquor). The pasted-up compound substrate K-3; the cable address of the column of a nitrocellulose expresses the following nitrocelluloses, respectively among the 3rd table with a thickness of 100 micrometers of a foaming polyethylene terephthalate sheet.

N-1; the cable address (Si1, Si4, Si21, Si23) of the column of a reactant silane compound expresses [whenever / 12 and nitrocellulose N-2; nitrification / of average degree of polymerization 40 / whenever / 12 and nitrocellulose N-3; nitrification / of average degree of polymerization 50 / whenever / 12 and nitrocellulose CN-1; nitrification / of average degree of polymerization 60 / whenever / 12 and nitrocellulose CN-2; nitrification / of average degree of polymerization 450] the compound mentioned to the 2nd table whenever [nitrification], respectively among 12 and the 3rd table of a nitrocellulose of average degree of polymerization 550.

[0081] In example 9 example 1, except changing a silicone rubber layer constituent into the following, others produced the photosensitive printing version similarly and evaluated similarly. Consequently, sensibility (95 cm/s) and ink impression nature (A) were obtained.

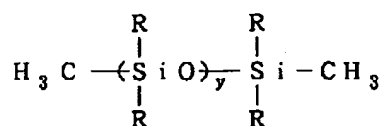
[0082]

[Silicone rubber layer constituent]

Organopolysiloxane which has at least two aliphatic series partial saturation radicals in 1 molecule: alpha, omega-divinyl poly dimethylsiloxane (Mw=12,000)

The 100 weight sections Organopolysiloxane which has at least two Si-H association in 1 molecule: The following alpha, omega-dimethylpolysiloxane [0083]

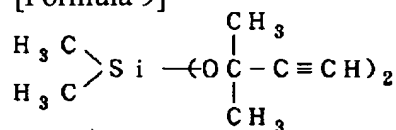
[Formula 8]



[0084]

(About 40% of the substituent R in a formula is a hydrogen atom, and about 60 remaining% is a methyl group moreover, $M_w = y$ indicates one or more integers to be 2,000) Seven weight sections Addition-reaction catalyst: Complex of chloroplatinic acid and a vinyl siloxane The 0.1 weight sections Concrete retarder: Bottom-type compound [0085]

[Formula 9]



0.005重量部

Spreading solvent: Isopar E (exon chemistry company make) The 900 weight sections [0086]

[Effect of the Invention] By this invention, when the effectiveness of ablation increased, sensibility can improve and the laser direct dampening water unnecessary photosensitivity lithography version which was further excellent in ink impression nature can be offered.

[Translation done.]